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PREPARATION AND CHARACTERIZATION OF MOLECULE-BASED  
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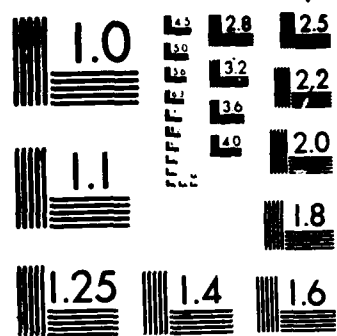
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TECHNICAL REPORT NO. 17

Preparation and Characterization of Molecule-Based Transistors  
with a 50 Nanometer Source-Drain Separation Using Shadow Deposition  
Techniques: Towards Faster, More Sensitive Molecule-Based Devices

by

E. Tracy Turner Jones, Oliver M. Chyan, and Mark S. Wrighton

Prepared for Publication

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Department of Chemistry  
Cambridge, MA 02139

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## Abstract

Preparation of Au microelectrode arrays having spacings of 50-100 nm and available electrode areas of  $<10^{-7}$  cm<sup>2</sup> is described. The dimensions are qualitatively smaller than previously reported and lead directly to faster switching and smaller switching energy for molecule-based transistors. Such microelectrodes can be functionalized with redox active polymers by oxidation of aniline to give polyaniline or by electrochemically assisted deposition of N,N'-bis(p-trimethoxysilylbenzyl)-4,4'-bipyridinium promoting Si-OMe hydrolysis to give the redox polymer (BPQ<sup>2+/+</sup>)<sub>n</sub>. The fabrication procedure begins with a microelectrode array consisting of eight, individually addressable Au microelectrodes each ~50 μm long x ~2.5 μm wide x ~0.1 μm thick with a spacing of ~1.5 μm between the microelectrodes. A line of sight e<sup>-</sup> beam deposition of ~50 nm of Au at a given angle, using the 0.1 μm thick microelectrodes to cast a shadow, can be used to close the spacing between microelectrodes to ~50 nm. A second line of sight deposition process at a slightly different angle, coats all but a small fraction of the Au with ~100 nm of insulating SiO<sub>2</sub> to give ultrasmall Au electrode areas. Molecule-based transistors using polyaniline or (BPQ<sup>2+/+</sup>)<sub>n</sub> as the channel material and a pair of microelectrodes as source and drain show that superior speed and sensitivity are the result of the ultrasmall electrode spacings and areas. The dimensions of the channel and the characteristics of the device are consistent with an amount of redox polymer corresponding to ~10<sup>-14</sup> moles of monomer, a factor of 10<sup>2</sup> less than used in previously reported molecule-based devices. The devices respond to a small fraction of a femtomole of e<sup>-</sup>'s (10<sup>-10</sup> C).

[Prepared for publication as a Communication to the Editor of the  
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PREPARATION AND CHARACTERIZATION OF MOLECULE-BASED TRANSISTORS  
WITH A 50 NANOMETER SOURCE-DRAIN SEPARATION USING SHADOW DEPOSITION  
TECHNIQUES: TOWARDS FASTER, MORE SENSITIVE MOLECULE-BASED DEVICES

E. Tracy Turner Jones, Oliver M. Chyan, Mark S. Wrighton\*

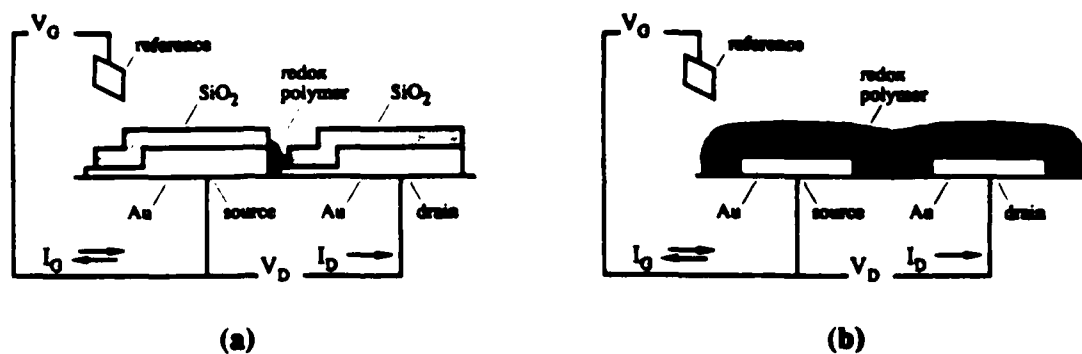
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Preparation of Au microelectrode arrays having spacings of 50-100 nm and available electrode areas of  $<10^{-7}$  cm<sup>2</sup> is described. The dimensions are qualitatively smaller than previously reported and lead directly to faster switching and smaller switching energy for molecule-based transistors. Such microelectrodes can be functionalized with redox active polymers by oxidation of aniline to give polyaniline or by electrochemically assisted deposition of N,N'-bis(p-trimethoxysilylbenzyl)-4,4'-bipyridinium promoting Si-OMe hydrolysis to give the redox polymer (BPQ<sup>2+/+</sup>)<sub>n</sub>. The fabrication procedure begins with a microelectrode array consisting of eight, individually addressable Au microelectrodes each ~50 μm long x ~2.5 μm wide x ~0.1 μm thick with a spacing of ~1.5 μm between the microelectrodes. A line of sight e<sup>-</sup> beam deposition of ~50 nm of Au at a given angle, using the 0.1 μm thick microelectrodes to cast a shadow, can be used to close the spacing between microelectrodes to ~50 nm. A second line of sight deposition process at a slightly different angle, coats all but a small fraction of the Au with ~100 nm of insulating SiO<sub>2</sub> to give ultrasmall Au electrode areas. Molecule-based transistors using polyaniline or (BPQ<sup>2+/+</sup>)<sub>n</sub> as the channel material and a pair of microelectrodes as source and drain show that superior speed and sensitivity are the result of the ultrasmall electrode spacings and areas. The dimensions of the channel and the characteristics of the device are consistent with an amount of redox polymer corresponding to ~10<sup>-14</sup> moles of monomer, a factor of 10<sup>2</sup> less than used in previously reported molecule-based devices. The devices respond to a small fraction of a femtomole of e<sup>-</sup>'s (10<sup>-10</sup> C).

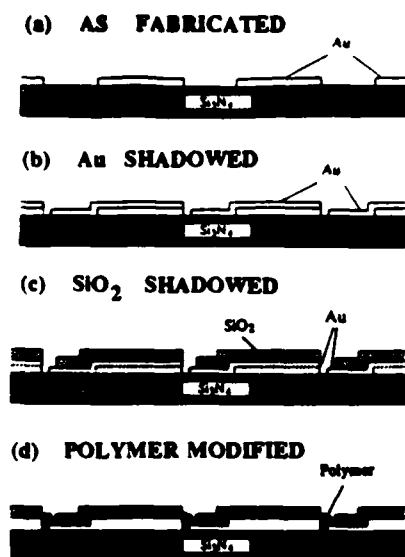
We report preparation and characterization of the molecule-based transistor in Scheme Ia having a significantly smaller ( $\sim 50$  nm vs.  $1.5$   $\mu\text{m}$ ) source-drain separation and smaller ( $10^{-14}$  moles vs.  $10^{-12}$  moles) amount of redox polymer comprising the channel compared to previously reported<sup>1</sup> devices like that in Scheme Ib. The new microstructure with 50 nm source-



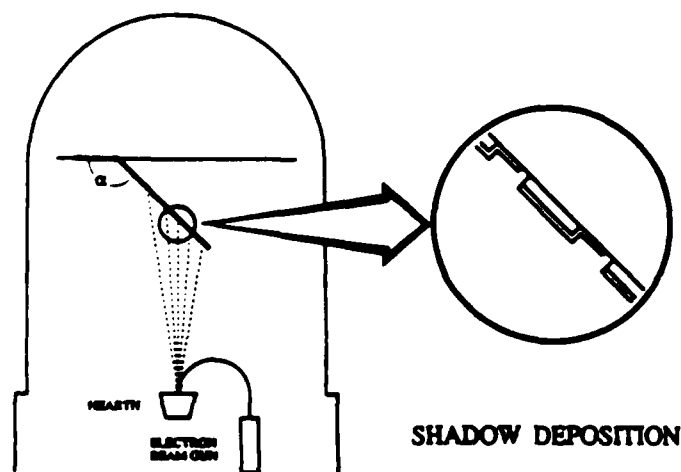
Scheme I (a) Device structure reported here and (b) previously.<sup>1d</sup>

drain spacing can be prepared by shadow deposition techniques<sup>2</sup> avoiding need for X-ray<sup>3</sup> or e<sup>-</sup> beam<sup>4</sup> lithography. The 50 nm spacing for the open-faced sandwich structure rivals the smallest spacing achievable with conventional sandwich arrangements of electrode/polymer/electrode used to demonstrate the first "bilayer" assemblies.<sup>5</sup>

Scheme II shows the sequence used to prepare the new microstructure Scheme Ia. The procedure begins with a Si<sub>3</sub>N<sub>4</sub>-coated Si wafer of microelectrode arrays previously described.<sup>1a</sup> Each chip on the wafer consists of eight, individually addressable Au microelectrodes each  $\sim 50$   $\mu\text{m}$  long x  $2.5$   $\mu\text{m}$  wide x  $0.1$   $\mu\text{m}$  thick with spacings between microelectrodes of  $\sim 1.5$   $\mu\text{m}$ . The first step involves a line of sight e<sup>-</sup> beam deposition of 50 nm of Au onto the wafer at an angle  $\alpha$  as illustrated in Scheme III. Generally, prior



Scheme II. Fabrication sequence  
for a 50 nm device.



Scheme III. Shadow deposition  
apparatus.

to Au deposition 5 nm of Cr is deposited as an adhesion layer. The line of sight deposition of Au results in a larger ( $\sim 4 \mu\text{m}$  wide) microelectrode than the original ( $2.5 \mu\text{m}$  wide) but the spacing can be closed to 50 to 100 nm as established by scanning electron microscopy (SEM), Figure 1. Variation of  $\alpha$  gives rise to variation in the spacing in a manner consistent with the length of the expected shadow. From SEM it is evident that imperfections on the edges of the original microelectrodes give rise to uneven spacings between the microelectrodes after shadow deposition. Indeed, the shadows accurately "image" the imperfections in a straightforward manner. Spacings cited here are "average" values.

The larger microelectrodes formed by shadow deposition of Au have the disadvantage that the absolute amount of electroactive area is relatively large. When redox material is electrochemically deposited, a device results that involves a much larger amount of active material than required to span the

50 nm spacing. A second shadow deposition process, Scheme II, line of sight  $e^-$  beam deposition of 100 nm of  $\text{SiO}_2$  at an angle  $\alpha$  smaller than for the Au deposition step, covers the majority of the exposed Au with an insulator, Figure 1. The result is a set of closely-spaced (50-100 nm) microelectrodes with ultrasmall electrode areas. The total microelectrode area available depends on the original microelectrode thickness,  $\alpha$  for  $\text{SiO}_2$  deposition, and the thickness of the shadow deposited Au. Typical area available is estimated to be below  $10^{-7} \text{ cm}^2$  per microelectrode. Figure 1 includes SEM showing a closely-spaced pair of microelectrodes that are the product of the shadow deposition of Au followed by  $\text{SiO}_2$ . Electrochemical deposition of  $(\text{BPQ}^{2+}/+)_n$ ,<sup>6</sup> from N,N'-bis(p-trimethoxysilylbenzyl)-4,4'-bipyridinium, or polyaniline<sup>1d,7</sup> onto the microfabricated structure shows that the  $\text{SiO}_2$  is an effective insulator and that the exposed Au is electrochemically active. SEM establishes polymer to be deposited mainly in the 50 nm channel region as in Scheme Ia. Electrochemical characterization of the system shows that the amount of polymer needed to make a connection is  $<10^{-14}$  moles of  $\text{BPQ}^{2+}$  units as established by the integration of a cyclic voltammogram associated with the  $\text{BPQ}^{2+} \rightleftharpoons \text{BPQ}^+$  interconversion for microelectrodes connected by the  $(\text{BPQ}^{2+}/+)_n$  polymer. These data show that  $10^{-2}$  times the amount of  $(\text{BPQ}^{2+}/+)_n$  is needed in comparison to the original microelectrode array.

Smaller microelectrode spacing and smaller polymer volume mean that molecule-based transistors require less energy for switching and can be switched more rapidly.<sup>1d</sup> Polyaniline-based transistors, Scheme Ia, with 50-100 nm source-drain separation have been demonstrated to switch from off to maximum on by passing  $<10^{-9} \text{ C}$ ,  $10^{-2}$  times the charge needed with the original dimensions.<sup>1d</sup> Figure 2 includes an electrochemical characterization of the polyaniline connecting two microelectrodes in that the  $I_G$  vs.  $V_G$  is in essence a cyclic

voltammogram with a sinusoidal variation in voltage. Figure 2 also reveals the change in conductivity accompanying cyclic oxidation/reduction as reflected in variation in  $I_D$  as  $V_G$  is varied. The data demonstrate power gain at frequencies exceeding 10 kHz almost  $10^2$  times higher than for a control device with a  $1.5 \mu\text{m}$  10 kHz the device turns on to nearly the same extent as at 1 Hz. The polyaniline device shows an easily detected variation in drain current,  $I_D$ , for flow of only  $10^{-12}$  C in the gate circuit accompanying  $\Delta V_G$  in the  $V_G$  region of maximum transconductance. Thus, the device can respond to a small fraction of a femtomole ( $10^{-10}$  C) of charge.

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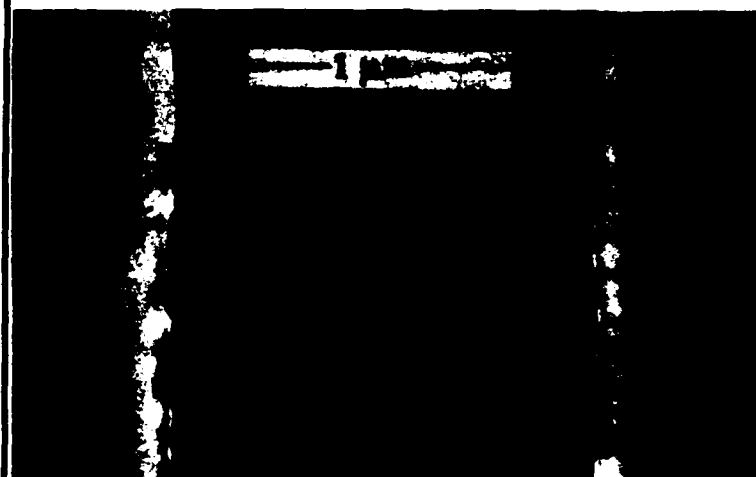
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## Figures

Figure 1. Scanning electron micrographs of a pair of microelectrodes at different stages of the fabrication sequence, Scheme II. (a) Original microelectrodes with 1.5  $\mu\text{m}$  spacing. (b) Gap closed to 50-70 nm by shadow deposition of Cr and Au. (c) Electroactive area of previously widened microelectrodes reduced upon shadow deposition of insulating  $\text{SiO}_2$  layer. Uneven spacing reflects original imperfections on the edge of the left microelectrode.

Figure 2. Gate potential ( $V_G$ ), gate current ( $I_G$ ), and drain current ( $I_D$ ) at 10 kHz for an ultrasmall gap polyaniline-based transistor, drain voltage  $V_D = 100$  mV. Inset shows  $\log_{10}$  (amplification) vs.  $\log_{10}$  (frequency) of 1.5  $\mu\text{m}$  gap ( ) vs. 70 nm gap ( ) polyaniline-based transistor, Scheme I. Blank experiments (no polyaniline on microelectrodes) show that the  $I_G$  and  $I_D$  measured for the polyaniline-based device are principally (>99 %) due to oxidation/reduction and resulting changes in conductivity of polyaniline

(a) AS FABRICATED



Au

Si<sub>3</sub>N<sub>4</sub>

Au

(b) Au SHADOWED



Au

Si<sub>3</sub>N<sub>4</sub>

Au

(c) SiO<sub>2</sub> SHADOWED

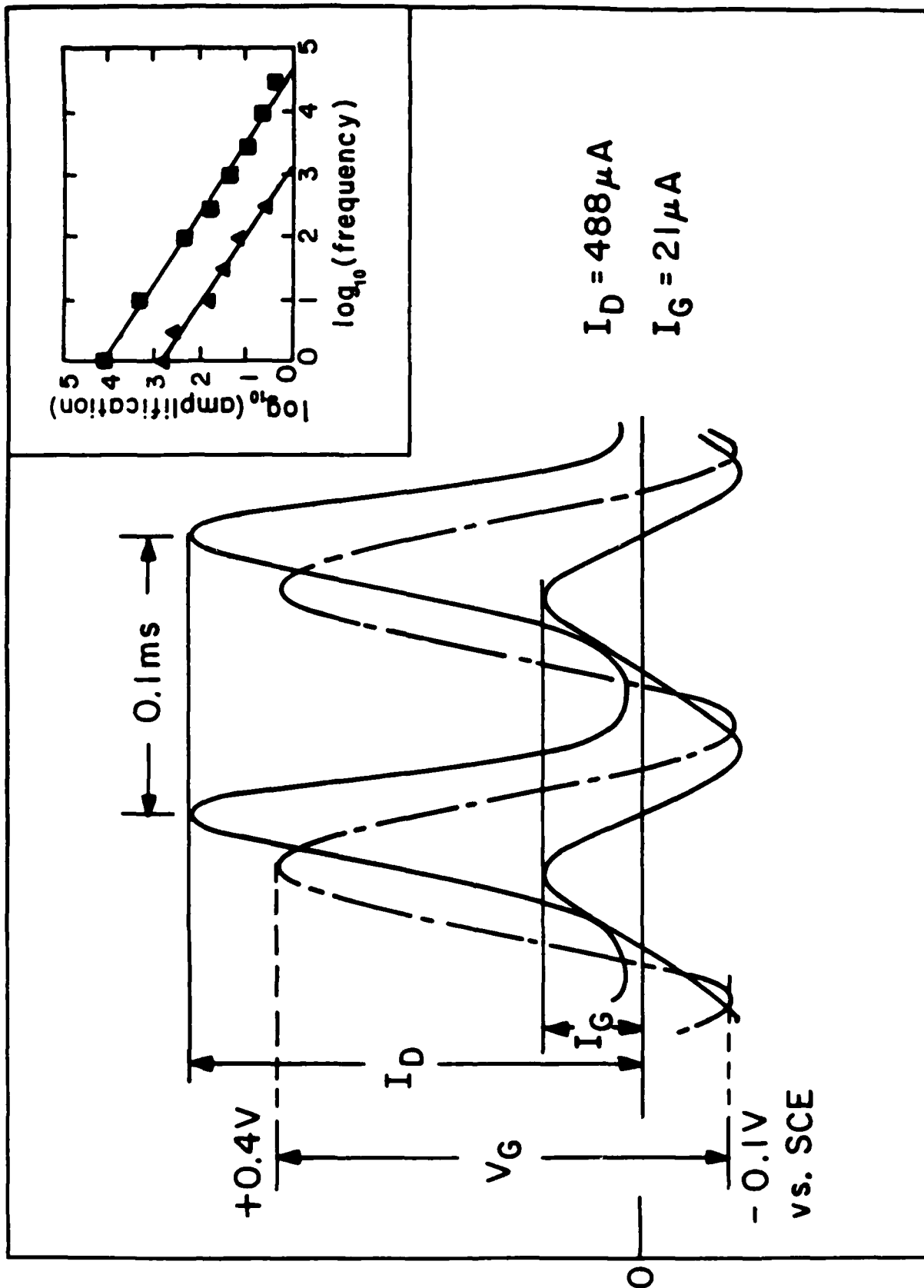


SiO<sub>2</sub>

Si<sub>3</sub>N<sub>4</sub>

Au

SiO<sub>2</sub>



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